

Kondo effect of a Co atom on Cu(111) in contact with an Fe tip

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Single Co atoms, which exhibit a Kondo effect on Cu(111), are contacted with Cu and Fe tips in a low-temperature scanning tunneling microscope. With Fe tips, the Kondo effect persists with the Abrikosov-Suhl resonance significantly broadened. In contrast, for Cu-covered W tips, the resonance width remains almost constant throughout the tunneling and contact ranges. The distinct changes of the line width are interpreted in terms of modifications of the Co d state occupation owing to hybridization with the tip apex atoms.

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The Kondo effect, one of the key correlation effects in condensed matter physics, results from scattering of conduction electrons from a localized half-filled d or f electron level. Below a characteristic Kondo temperature (T_K) the excitation spectrum of the local impurity exhibits an Abrikosov-Suhl resonance at the Fermi level with a width $k_B T_K$ (k_B : Boltzmann's constant). Its lineshape is susceptible to changes of the local environment of the impurity and to magnetic fields. In external magnetic fields, Zeeman splitting of the electron level involved in the Kondo effect leads to splitting of the resonance.¹⁻⁴ Additional effects occur in magnetic nanostructures. Interactions between two Kondo impurities mediated by itinerant electrons may result in a complete or partial suppression or a splitting of the resonance, depending on the relative magnitudes of the Kondo energy scales of the individual impurities and the interaction energy.⁵⁻¹² A splitting of the resonance observed from impurities at ferromagnetic islands has been attributed to exchange interaction.¹³ Surprisingly, a Kondo effect has even been reported from atomic point contacts between ferromagnetic electrodes, which implies a significantly modified magnetism.¹⁴ Recent theoretical work showed that ferromagnetic coupling between nearly ferromagnetic Pd or Pt electrodes and a magnetic impurity may lead to an Abrikosov-Suhl resonance or a pseudogap at the Fermi level depending on the coupling strength.¹⁵ The Abrikosov-Suhl resonance may also be tuned by controlling the hybridization of a magnetic impurity with nonmagnetic neighbors.¹⁶⁻¹⁸

Here, we use a scanning tunneling microscope (STM) to directly compare the evolution of the Kondo effect of a single Co atom adsorbed on Cu(111) upon approaching a ferromagnetic Fe and a nonmagnetic Cu-covered W tip until contact is reached. We find that hybridization effects have to be considered for ferromagnetic tips to adequately describe the line shape of the Abrikosov-Suhl resonance. Approaching the adsorbed atom (adatom) with Fe tips shows that the Abrikosov-Suhl resonance persists at contact. No splitting is resolved, but the resonance is significantly broadened. In contrast, Cu-covered W tips leave the resonance almost unaffected throughout the tunneling and contact ranges. As the resonance line

shape is linked to the occupation of the Co d states, these results may be interpreted in terms of different hybridizations between the Co atom and the tip materials without involving magnetic interactions. So far, little is known from experiments about the electronic states of an atom or a molecule in contact with two electrodes.^{19,20} This modest data base on basic electronic (and structural) properties is in some contrast to a wealth of theoretical results on, *e. g.*, energy-resolved conductances. The detour via the Kondo effect may therefore turn out to be useful in honing electronic structure calculations, which underly the transport results.

The experiments were performed with a home-made STM operated at 7 K and in ultrahigh vacuum (10^{-9} Pa). Tips were fabricated from pure polycrystalline W and Fe wires by chemical etching in solutions of NaOH and HCl, respectively. Sample surfaces and Fe and W tips were cleaned by Ar^+ bombardment and annealing. Prior to mounting to the cold STM Fe tips were placed close to a CoSm permanent magnet to induce a magnetization along the long tip axis. Co atoms were deposited onto the Cu(111) surface at ≈ 10 K using an electron beam evaporator and an evaporant of 99.99 % purity. Spectroscopy of the differential conductance (dI/dV) was performed by a lock-in technique with a modulation of $1 \text{ mV}_{\text{rms}}$ and 8 kHz added to the sample voltage. Conductance versus tip displacement curves were acquired by moving the tip towards the adatom at a velocity of 50 \AA s^{-1} and simultaneously recording the current. The cleanliness of the tips was checked by dI/dV spectra, which exclusively showed the spectroscopic signature of the Cu(111) surface state on pristine Cu(111). Particular care was taken to avoid coating of the Fe tip apex with substrate material.

Figure 1(a) shows the evolution of the conductance of a single-Co junction upon approaching (from right to left) a Fe tip to the individual Co adatom on Cu(111). The tunneling range is characterized by an exponential variation of the conductance with the displacement, Δz ($0 \text{ \AA} > \Delta z > -2.65 \text{ \AA}$). The transition from tunneling to contact takes place within $\approx 0.35 \text{ \AA}$ ($-2.65 \text{ \AA} > \Delta z > -3 \text{ \AA}$). For $\Delta z < -3 \text{ \AA}$ the contact range is reached and the conductance rises slowly with further tip displacement. A contact conductance, G_c , is defined as the intersection of lin-

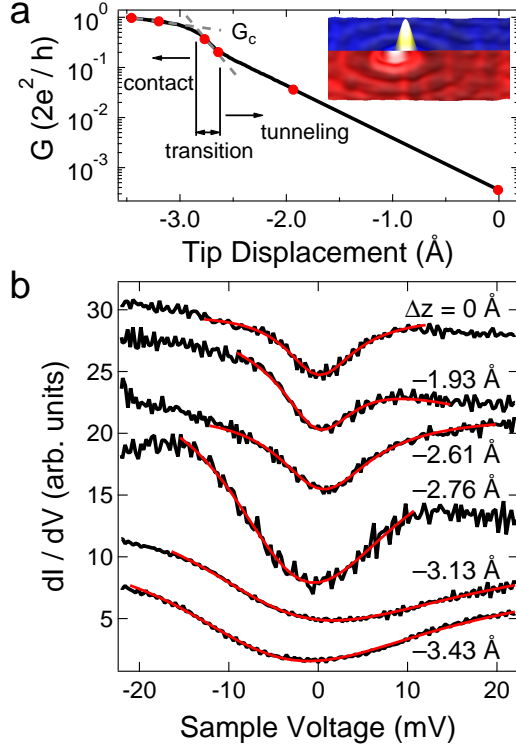


FIG. 1. (Color online) (a) Conductance of a Co adatom on Cu(111) approached by a Fe tip. Tunneling, transition and contact ranges are indicated. The conductance trace between 0 and ≈ -2 Å is an exponential extrapolation of tunneling conductance in the displacement range from ≈ -2 to -2.5 Å. The contact conductance, G_c , is defined by the intersection of linear fits (dashed lines) to conductance data in the contact and transition ranges. Zero displacement is defined by feedback loop parameters of 33 mV and 1 nA. Inset: Pseudo-three-dimensional presentation of a constant-current STM image of a single Co adatom on Cu (111) ($8 \text{ Å} \times 8 \text{ Å}$, 33 mV, 1 nA). (b) Spectra of dI/dV acquired at junction conductances indicated by dots on the conductance trace in (a). Solid lines are fits of Fano line shapes to experimental data.

ear fits to conductance data in the contact and transition ranges.²¹ The single-Co contact exhibits a conductance of $G_c \approx (0.70 \pm 0.05) G_0$ ($G_0 = 2e^2/h$, e : electron charge, h : Planck's constant). This value is lower than the quantum of conductance, G_0 , which has been obtained for Co adatoms contacted with nonmagnetic electrodes.^{16,17} However, it is in agreement with the contact conductance measured from a single Co adatom contacted by a ferromagnetic Ni tip and a Cu(111) surface.²²

In a next step, the tip position was frozen at characteristic displacements [indicated by dots on the conductance trace in Fig. 1(a)] and spectra of dI/dV were acquired. The resulting data are presented in Fig. 1(b). The three top spectra were recorded in the tunneling range, the fourth spectrum in the transition between tunneling and contact, and the two lower spectra were acquired in the contact range. Prior to and after contact the Co adatom

was imaged and dI/dV spectroscopy was performed to detect possible modifications of structural or electronic properties of the junction. The spectroscopic signature of the Kondo effect is present in all dI/dV spectra and appears with a Fano line shape around zero voltage.^{23,24} While the tunneling spectra exhibit similar line shapes, the Abrikosov-Suhl resonance starts to broaden in the transition range and appears even wider in contact. The observation of a broadened Abrikosov-Suhl resonance of the Co adatom in contact with a ferromagnetic Fe tip is surprising in the light of previous work that reported the disappearance or splitting of the resonance when the Kondo impurity was close to magnetic atoms^{5,11,12} or nanostructures.¹³ The only work showing the presence of the (unsplit) Abrikosov-Suhl resonance in ferromagnetic point contacts has been reported by Reyes *et al.*¹⁴ From a statistical analysis of dI/dV spectra the authors of Ref. 14 inferred that the Kondo effect is present in ferromagnetic Fe, Co and Ni contacts. They suggested that reduced symmetry and the decreased coordination of the atom in the contact may favor the observation of the Kondo effect.

To analyse the modifications of the Abrikosov-Suhl resonance at contact, a Fano line shape may be used.^{16,25} The resulting parameters, *i. e.*, Kondo temperature T_K , resonance energy ϵ_K and asymmetry parameter q , are presented in Fig. 2 for spectra acquired with a Fe (open symbols) and a Cu-covered W (filled triangles) tip. In the tunneling range ($\Delta z > -2.65$ Å), these parameters are almost equal and constant for both tip materials, which reflects that the interaction between the tip and the sample are negligible in this conductance range. Starting from the transition range, however, Fe and Cu-covered W tips lead to strikingly different results. For Fe tips, all parameters start to deviate from their tunneling range values. T_K increases from ≈ 60 K to ≈ 130 K, q increases from ≈ 0.05 to ≈ 0.25 , and the resonance energy drops from ≈ 0 to ≈ -3 meV. At contact, this trend is continued and T_K reaches ≈ 200 K, $q \approx 0.3 - 0.4$ and $\epsilon_K \approx -6$ meV. For Cu-coated W tips all parameters are essentially constant throughout the tunneling, transition and contact ranges in agreement with previous results.¹⁷ Obviously, the chemical identity of the tip apex atom determines the degree of hybridization. The splitting of the resonance due to the magnetic dipole field of the Fe tip at the adatom site is too low to explain the observed broadening. Estimating the dipole field at contact as $H \approx 1$ T,²⁶ the splitting is of the order of $2g\mu_B H \approx 0.2$ meV (g : Landé factor, μ_B : Bohr's magneton),²⁷ which is more than one order of magnitude lower than $k_B T_K$ with $T_K \approx 60$ K.

The asymmetry parameter q describes the coupling of the probe to the discrete Co d state and the continuum of sp conduction electrons.^{23,24} The considerable increase of q upon hybridization of the Co adatom with the Fe tip suggests that additional tip states couple to the Co d levels. Indeed, ferromagnetic Fe exhibits d bands at the Fermi level,²⁸ which may hybridize with the adatom

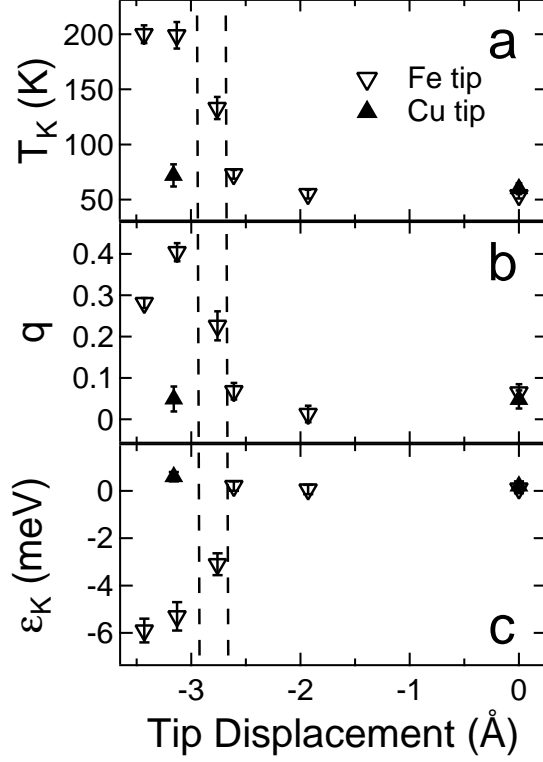


FIG. 2. Kondo temperature T_K , asymmetry factor q and resonance energy ϵ_K for a Co adatom on Cu(111) contacted with a Fe (open symbols) and a Cu-covered W (filled triangles) tip as a function of the tip displacement. Uncertainty margins result from fitting a variety of dI/dV spectra. Dashed lines separate tunneling, transition and contact ranges as introduced in Fig. 1(a).

d states at contact. The d bands of Cu, however, are well below the Fermi energy²⁹ and thus no additional hybridization is expected in agreement with an almost constant asymmetry parameter. In the tunneling range, owing to the stronger spatial decay of d states compared to s states,³⁰ only s states participate in the hybridization and thus lead to a similar q parameter for Fe and Cu-covered W tips.

The different hybridization may be described by the Co d state occupation number, n_d , which is related to the resonance energy and the Kondo temperature via³¹

$$n_d = 1 - \frac{2}{\pi} \tan^{-1} \left(\frac{\epsilon_K}{k_B T_K} \right) \quad (1)$$

and thus may be estimated from the extracted fit parameters. In the following we assume that only a single Co d level participates in the hybridization. This assumption appears to be reasonable in the light of a recent theoretical study of a Co adatom on Au(111).³² Owing to $sp-d$ hybridization four Co d orbitals are completely occupied while the orbital which is responsible for the Kondo effect is partly filled with 0.8 electrons.³² Empty,

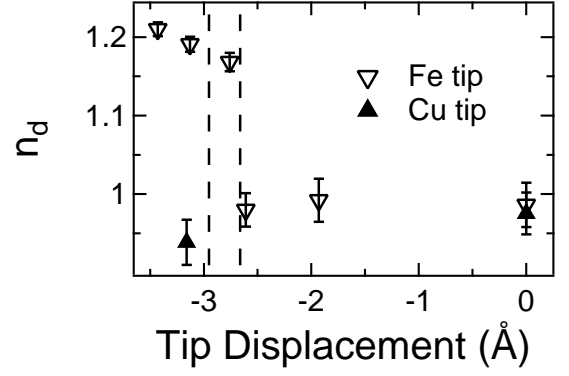


FIG. 3. Occupation number of Co d states, n_d , as a function of the tip displacement. Open (filled) triangles present data for a Co adatom on Cu(111) contacted by a Fe (Cu-covered W) tip. n_d has been calculated using Eq. (1) with fit parameters ϵ_K and T_K (Fig. 2). Dashed lines separate tunneling, transition and contact ranges as introduced in Fig. 1(a).

half-filled, and filled d levels correspond to $n_d = 0, 1$, and 2, respectively. Figure 3 shows n_d according to Eq. (1) as a function of the tip displacement for Fe (open symbols) and Cu-covered W (filled triangles) tips. Clearly, n_d changes upon hybridization of the Co adatom with the Fe tip apex atom from ≈ 0.98 (average value in the tunneling range) to ≈ 1.2 (contact) while it stays almost constant for the Cu-covered W tip (≈ 0.98). A value of ≈ 0.98 is in good agreement with the occupation number obtained for Co adatoms on Cu(111) in the tunneling range, while $n_d \approx 1.2$ comes close to the value of a Co adatom on Cu(100).³³

The influence of n_d on T_K may be evaluated according to³²

$$k_B T_K \approx \sqrt{\frac{\Delta U}{2}} \exp \left(-\frac{\pi U}{2 \Delta} \left| \frac{3}{2} - n_d \right| \left| \frac{1}{2} - n_d \right| \right), \quad (2)$$

where U is the on-site Coulomb repulsion and Δ the half width of the hybridized d level. Using Eq. (2) with $U = 2.4$ eV and $\Delta = 0.2$ eV as calculated for Co adatoms on Cu(100) in the tunneling range,¹⁶ a Kondo temperature of $T_K \approx 50$ K is obtained for $n_d = 0.98$. At contact, the on-site Coulomb repulsion is reduced to $U = 1.9$ eV as previously reported in Ref. 16. Together with the increased occupation number $n_d = 1.2$ at contact (Fig. 3) a Kondo temperature of $T_K \approx 200$ K is obtained. These values are in agreement with the measured Kondo temperatures in the tunneling and contact ranges [Fig. 2(a)]. Consequently, the experimentally observed variations of T_K , ϵ_K and q are compatible with variations of the Co d level occupation number upon hybridization with the tip and do not rely on a ferromagnetic exchange interaction between the tip apex and the adsorbed atom. The occupation number may likewise be altered by a modification of the hybridization with the substrate. At contact, owing to adhesive forces between the tip and the adatom,

the adatom is lifted from the surface,^{17,34} which in turn affects the d level occupation.

In conclusion, the Kondo effect of a single magnetic impurity has been used to monitor the hybridization of the impurity with Cu and Fe tips. The degree of hy-

bridization has been inferred from the impurity d level occupation number, which in turn has been extracted from the width of the Abrikosov-Suhl resonance.

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